BEST AVAILABLE COPY

PCT/EP2004/006806

PATENTS • DESIGNS • COPYRIGHT • TRADE MARKS
The Patent Office

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 26 AUG 2004
WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Signed Andrew Gerrard

Dated 22 June 2004

Patents Form 1/77

Patents Act 1977
(Rule 16)

05JUL03 E820215-1 C03022
P01/7700 0.00-0315685.8

- 4 JUL 2003

THE PATENT OFFICE
J
- 4 JUL 2003
NEWPORT

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

SPE 02/15

2. Patent application number
(The Patent Office will fill in this part)

0315685.8

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

SOLVAY POLYOLEFINS EUROPE-BELGIUM
(SOCIETE ANONYME)
rue du Prince Albert 44
1050 Bruxelles
BELGIUM

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

08495202001

4. Title of the invention

POLYETHYLENE PIPE RESINS

5. Name of your agent *(if you have one)*

SMITH, Julian Philip Howard

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

BP INTERNATIONAL LIMITED
PATENTS & AGREEMENTS
CHERTSEY ROAD
SUNBURY-ON-THAMES
MIDDLESEX
TW16 7LN
UNITED KINGDOM

Patents ADP number *(if you know it)*

00018556002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

YES

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	13
Claim *(s)*	2
Abstract	–
Drawing *(s)*	7 + 7

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 03.07.2003

smith, Julian Philip Howard

12. Name and daytime telephone number of person to contact in the United Kingdom 01932 764092

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) *If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.*

b) *Write your answers in capital letters using black ink or you may type them.*

c) *If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*

d) *If you have answered 'Yes' Patents Form 7/77 will need to be filed.*

e) *Once you have filled in the form you must remember to sign and date it.*

f) *For details of the fee and ways to pay please contact the Patent Office.*

POLYETHYLENE PIPE RESINS

The present invention relates to polyethylene resins, more particularly those suitable for use as pipe resins, and to a process for producing such resins. The present invention also relates to the use of polyethylene compounds comprising such resins for the manufacture of pipes and fittings, and to such pipes and fittings themselves.

Polyethylene resins are known for the production of pipes and fittings. Pipe resins require high stiffness (creep rupture strength), combined with a high resistance against slow crack growth as well as resistance to crack propagation yielding impact toughness. However, there is the need to improve the creep rupture strength of currently available pipe resins, keeping the resistance against slow crack growth and the rapid crack propagation at least at a constant level. This would permit an increase in the pressure rating of such pipes.

Polyethylene pipes are widely used as they are lightweight and can be easily assembled by fusion welding. Polyethylene pipes also have a good flexibility and impact resistance, and are corrosion free. Unless polyethylene pipes are reinforced, they are however limited in their hydrostatic resistance by the inherent low yield strength of polyethylene. It is generally accepted that the higher the density of the polyethylene, the higher will be the long-term hydrostatic strength. Pipe resins are known in the art which are referred to by the names "PE 80" and "PE 100". These classifications are described in ISO 9080 and ISO 12162. Extrapolation according to ISO 9080 shows that they have an extrapolated 20°C / 50 years stress at a lower prediction level (97.5% confidence level - "LPL") of at least 8 MPa [PE 80] and 10 MPa [PE 100]. The term "pressure pipe" in this specification refers to a pipe having a pressure rating of PE 80 and above.

There is a need in the art for polyethylene pipe resins which exceed the above test requirements. Currently, for polyethylene the highest hydrostatic strength which can be

tolerated based on an extrapolation of the hoop stress/lifetime relationship at a temperature of 20°C for a period of 50 years is an LPL of 10 MPa. This corresponds to a PE 100 resin. The density of the current basic powder used in the production of a PE 100 compound is close to 0.950 g/cm^3 (typically from 0.949 to 0.951 g/cm^3). Such polyethylene resins containing conventional amounts of black pigments have densities from about 0.958 to 0.960 g/cm^3. There is now a desire in the art to produce a resin which when transformed into the form of a pipe, is capable of withstanding an LPL stress of 12.5 MPa at a temperature of 20°C for a period of 50 years. Using the current terminology in the art, such a resin would be known as a "PE 125 grade" resin. Currently no such resins are commercially available.

Certain bimodal polyethylene resins are known to have very good hydrostatic strength. For example, WO 02/34829 discloses a polyethylene resin comprising from 35 to 49 wt% of a first polyethylene fraction of high molecular weight and from 51 to 65 wt% of a second polyethylene fraction of low molecular weight, the first polyethylene fraction comprising a linear low density polyethylene having a density of up to 0.928 g/cm^3, and an HLMI of less than 0.6 g/10min and the second polyethylene fraction comprising a high density polyethylene having a density of at least 0.969 g/cm^3 and an MI_2 of greater than 100 g/10min, and the polyethylene resin having a density of greater than 0.951 g/cm^3 and an HLMI of from 1 to 100 g/10min.

We have found that by incorporating an ionomer into polyethylene, it is possible to obtain resins with superior properties to those of equivalent known resins. Accordingly, in its broadest aspect the present invention provides a pressure pipe resin comprising from 90 to 99.9 wt%, based on the total weight of the resin, of a polyethylene, and from 0.1 to 10 wt%, based on the total weight of the blend, of an ionomer.

Preferably the polyethylene is multimodal. By "multimodal" polyethylene is meant polyethylene having at least two components of different molecular weights and compositions (ie comonomer content). More preferably the resin is bimodal, by which is meant that it comprises two components of different molecular weights, one having a higher relative molecular weight than the other of the two components and compositions (ie comonomer content). The resin usually has a density of at least 0.930 g/cm^3.

More preferably the pressure pipe resin comprises a blend of (a) a polyethylene resin comprising from 35 to 60 wt% of a higher molecular weight fraction having a density of up to 0.930 g/cm^3 and from 40 to 65 wt% of a lower molecular weight fraction having a density of at least 0.965 g/cm^3, and (b) from 0.1 to 10 wt%, based on the total weight of the blend, of an

ionomer.

By "ionomer" is meant a polymeric composition obtained by the introduction of acidic groups at molar concentrations below 10% into an addition polymer, followed by partial neutralization with metal cations or amines, such as a compound of the monovalent, divalent and/or trivalent metals of Group I, II, IV-A and VIIIB of the periodic table of the elements.

Preferred ionomers are derived from a copolymer of at least one alpha-olefin and at least one ethylenically unsaturated carboxylic acid and/or anhydride. Suitable alpha-olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3-methylbutene, and the like. Suitable carboxylic acids and anhydrides include acrylic acid, methacrylic acid, ethacrylic acid, maleic acid, fumaric acid, maleic anhydride, and the like. The foregoing copolymers generally contain from about 0.2 to about 10 mole percent, and preferably from about 0.5 to about 8 mole percent, carboxylic acid groups.

Particular examples of such copolymers include ethylene-maleic anhydride copolymers, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, ethylene-itaconic acid copolymers, ethylene-methyl hydrogen maleate copolymers, ethylene-maleic acid copolymers, ethylene-acrylic acid copolymers, ethylene-methacrylate copolymers, ethylene-methacrylic acid-ethacrylate copolymers, ethylene-itaconic acid-methacrylate copolymers, ethylene-itaconic acid-methacrylate copolymers, ethylene-methyl hydrogen maleate-ethyl acrylate copolymers, ethylene-methacrylic acid-vinyl acetate copolymers, ethylene-acrylic acid copolymers, ethylene-acrylic acid-vinyl alcohol copolymers, ethylene-acrylic acid-carbon monoxide copolymers, ethylene-propylene-acrylic acid copolymers, ethylene-methacrylic acid-acrylonitrile copolymers, ethylene-fumaric acid-vinyl methyl ether copolymers, ethylene-vinyl chloride-acrylic acid copolymers, ethylene-vinylidene chloride-acrylic acid copolymers, ethylene-vinylidene chloride-acrylic acid copolymers, ethylene-vinyl fluoridemethacrylic acid copolymers and ethylene-chlorotrifluoroethlyene-methacrylic acid copolymers.

Preferred ionomers are obtained by reacting the foregoing copolymers with a sufficient amount of metal ions as to neutralize at least some portion of the acid groups, preferably at least about 5 percent by weight and preferably from about 20 to about 100 percent by weight, of the acid groups present. Suitable metal ions include Na^+, K^+, Li^+, Cs^+, Rb^+ Hg^+, Cu^+, Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Cu^{++}, Cd^{++}, Hg^{++}, Sn^{++}, Pb^{++}, Fe^{++}, Co^{++}, Ni^{++}, Zn^{++}, Al^{+++}, Sc^{+++} and Y^{+++}. Preferred metals suitable for neutralizing the copolymers used herein are the alkali metals, particularly cations such as sodium, lithium and potassium and alkaline earth metals, and in

particular cations such as calcium, magnesium and zinc. One or more ionomers may be used in the present invention.

Preferred ionomers include Surlyn® ionomers, such as zinc or sodium salts of an ethylene and methacrylic acid copolymer. Surlyn® ionomers may be obtained from E.I. Dupont de Nemours & Company, Wilmington, Del.

Other preferred ionomers include Priex® ionomers, available from Solvay, which are metal salts of an ethylene and grafted maleic anhydride copolymer.

The preferred quantity of ionomer in the blend is between 0.5 and 6 wt% based on the total weight of the blend, more preferably between 1 and 5 wt%.

Generally for all embodiments of the polyethylene resin utilised in the invention, the low molecular weight fraction of the resin preferably has a density of from 0.970 to 0.990 g/cm^3, more preferably from 0.971 to 0.980 g/cm^3, and an MI_2 from 200 to 1000 g/10min, more preferably from 300 to 1000 g/10min.

Preferably, for the high molecular weight fraction, the density is from 0.908 to 0.930 g/cm^3, more preferably from 0.912 to 0.928 g/cm^3 and particularly from 0.915 to 0.922 g/cm^3. The HLMI is preferably from 0.001 to 0.5 g/10min, more preferably from 0.01 to 0.35 g/10min, with most preferred ranges from 0.02 to 0.15 g/10min and more particularly from 0.02 to 0.1 g/10min.

In this specification the melt index MI_2 and high load melt index HLMI are measured in accordance with ASTM D-1238 at 190°C with respective loads of 2.16 and 21.6 kg. For MI_2, this standard requires an 8/2 die, although for convenience measurements have also been made using an 8/1 die, which gives values slightly more than 0.05 of those with the 8/2 die. In this specification the density is measured in accordance with ISO 1183.

For the low molecular weight polyethylene fraction, the polydispersity index D (represented by the ratio Mw/Mn as determined by gel permeation chromatography (GPC)) is preferably from 2 to 6. For the linear low density polyethylene fraction of high molecular weight the value of polydispersity index D is preferably from 2 to 6. Preferably, the overall polyethylene resin has a molecular weight distribution Mw/Mn from 8 to 40.

Preferably, the high molecular weight fraction is a copolymer of ethylene and another alpha-olefin containing from 3 to 12 carbon atoms. More preferably, it is a copolymer of ethylene and butene, methylpentene, hexene and/or octene.

Preferably, the low molecular weight fraction is an ethylene homopolymer.

In one embodiment of the present invention, the polyethylene resin

preferably comprises from 35 to 49 wt% of a first polyethylene fraction of high molecular weight, and from 51 to 65 wt% of a second polyethylene fraction of low molecular weight, the first polyethylene fraction comprising a linear low density polyethylene having a density of up to 0.928g/cm^3 and an HLMI of less than 0.6g/10min, and the second polyethylene fraction comprising a high density polyethylene having a density of at least 0.969g/cm^3 and an MI_2 of greater than 100g/10min, and the polyethylene resin having a density of greater than 0.940g/cm^3 and an HLMI of from 1 to 100 g/10min.

In this embodiment, the resin utilised in the blend with the ionomer preferably comprises at least 55wt% of the second polyethylene fraction of low molecular weight, most preferably at least 56wt%. It preferably comprises not more than 45wt% of the first polyethylene fraction of high molecular weight, more preferably at most 44wt%.

Preferably in this embodiment, the density of the polyethylene resin utilised in the blend is from 0.952 to 0.960g/cm^3, more preferably from 0.954 to 0.958g/cm^3. Its HLMI is preferably from 5 to 90 g/10min, more preferably from 10 to 80 g/10min.

In another preferred embodiment of the invention, the polyethylene resin comprises from 44 to 56 wt% of a high molecular weight polyethylene fraction, and from 44 to 56 wt% of a low molecular weight polyethylene fraction;

the high molecular weight polyethylene fraction comprising a linear low density polyethylene having a density of from 0.913 to 0.923g/cm^3, and an HLMI of from 0.02 to 0.2 g/10min;

and the low molecular weight polyethylene fraction comprising a high density polyethylene having a density of at least 0.969 g/cm^3 and an MI_2 of greater than 100 g/10min,

wherein the relationship between the density D of the resin in g/cm^3 and the weight fraction of the low molecular weight fraction P_1 is defined by $0.055P_1 + 0.916 < D < 0.034P_1 + 0.937$.

In this embodiment, the density D of the polyethylene resin is preferably at least 0.945g/cm^3, more preferably from 0.945 to 0.955 g/cm^3, and particularly from 0.948 to 0.954 g/cm^3. It is also preferred that the relationship between the density D of the resin in g/cm^3 and the weight fraction of the low molecular weight fraction P_1 is defined by $0.055P_1 + 0.919 < D < 0.034P_1 + 0.939$.

In this embodiment, the polyethylene resin preferably comprises less than 54 % by weight of the second polyethylene fraction of low molecular weight, most preferably between 48 and 53 weight %. It preferably comprises at least 46 % by weight of the first polyethylene

fraction of high molecular weight, most preferably at least 47 weight %. Its HLMI is preferably from 3 to 50 g/10min, more preferably from 5 to 25 g/10min.

The present invention further provides the use of a blend of a polyethylene resin as defined above and an ionomer for the manufacture of pressure pipes and fittings, and in a further aspect a pressure pipe or a fitting comprising the blend of the invention.

The present inventors have found that the pressure pipe resins produced in accordance with the invention exhibit a better creep resistance at low temperature than the currently obtainable PE 100 type resins while maintaining good slow crack growth resistance and impact strength. The resins according to the invention are therefore well suited for the manufacture of high pressure pipes and fittings. When used for the manufacture of pipes, the resins are most often blended with usual additives such as antioxidants, anti-acids and colourants.

The pipe resins of the invention show good creep resistance. Creep resistance is typically measured according to ISO 1167 on 32 mm diameter SDR11 pipes to determine the lifetime prior to failure at a temperature of 20°C and a stress of 13 MPa, 13.7 or 13.9 MPa.

The polyethylene resins utilised in the invention can themselves be prepared by different methods, such as melt blending, reactor in series configuration or single reactor with dual site catalysts. Preferably, the high density and low density fractions of the polyethylene resin are produced in at least two separate reactors, most preferably two such reactors in series. In such a case, the high density fraction is preferably prepared first, so that the low density fraction is prepared in the presence of the high density fraction. The resultant resin has a bimodal molecular weight distribution. The catalyst employed in the polymerisation process may be any catalyst(s) suitable for preparing the low and high density fractions. Preferably, the same catalyst produces both the high and low molecular weight fractions. For example, the catalyst may be a chromium catalyst, a Ziegler-Natta catalyst, a metallocene catalyst or a transition metal catalyst. Using a Ziegler catalyst, the polyethylene resins may be made as described in EP 897934A; using a metallocene catalyst, they may be made as described in the aforementioned WO 02/34829, or copending application EP 02076729.9.

The resins may be made using a metallocene catalyst system, which is preferably a bis-tetrahydroindenyl compound (THI). The use of such catalysts enables the production of both low and high density fractions having narrow molecular weight distributions. Preferably the catalyst system comprises (a) a metallocene catalyst component comprising a bis-tetrahydroindenyl compound of the general formula $(IndH_4)_2R''MQ_2$ in which each $IndH_4$ is

the same or different and is tetrahydroindenyl or substituted tetrahydroindenyl, R" is a bridge which comprises a C_1-C_4 alkylene radical, a dialkyl germanium or silicon or siloxane, or an alkyl phosphine or amine radical, which bridge is substituted or unsubstituted, M is a Group IV metal or vanadium and each Q is hydrocarbyl having 1 to 20 carbon atoms or halogen; and

(b) a cocatalyst which activates the catalyst component.

With the preferred bis-tetrahydroindenyl catalyst, each bis-tetrahydroindenyl compound may be substituted in the same way or differently from one another at one or more positions in the cyclopentadienyl ring, the cyclohexenyl ring and the ethylene bridge. Each substituent group may be independently chosen from those of formula XR_v in which X is chosen from group IVB, oxygen and nitrogen and each R is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms and v+1 is the valence of X. X is preferably C. If the cyclopentadienyl ring is substituted, its substituent groups must not be so bulky as to affect coordination of the olefin monomer to the metal M. Substituents on the cyclopentadienyl ring preferably have R as hydrogen or CH_3. More preferably, at least one and most preferably both cyclopentadienyl rings are unsubstituted.

In a particularly preferred embodiment, both indenyls are unsubstituted.

R" is preferably an ethylene bridge which is substituted or unsubstituted.

The metal M is preferably zirconium, hafnium or titanium, most preferably zirconium. Each Q is the same or different and may be a hydrocarbyl or hydrocarboxy radical having 1-20 carbon atoms or a halogen. Suitable hydrocarbyls include aryl, alkyl, alkenyl, alkylaryl or aryl alkyl. Each Q is preferably halogen. Ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride is a particularly preferred bis tetrahydroindenyl compound of the present invention.

The metallocene catalyst component used to produce the polyethylene resin utilised in the present invention can be prepared by any known method. A preferred preparation method is described in J. Organomet. Chem. 288, 63-67 (1985).

The cocatalyst which activates the metallocene catalyst component can be any cocatalyst known for this purpose such as an aluminium-containing cocatalyst, a boron-containing cocatalyst or a mixture of those. The aluminium-containing cocatalyst may comprise an alumoxane, an alkyl aluminium and/or a Lewis acid.

Ionomers such as those utilised in the present invention are commercially available, and may thus be made by well-known methods. An example of such a process is described in EP 1177229A.

The polyethylene resins are blended with ionomers by known methods. Typically, flakes of the polyethylene resin and ground ionomer pellets are blended in an extruder and then pelletised.

The invention will now be described in further detail with reference to the following non-limiting Examples.

EXAMPLES

PREPARATION OF BLENDS

Blends of an ionomer resin and three polyethylene resins were prepared. The ionomer resin was a zinc salt of an ethylene and maleic anhydride graft copolymer. The base polyethylene resin used for the preparation of the ionomer was of a textile grade typically having a density of 944 kg/m^3 and an MI_2 of 3.5 g/10min, and the maleic anhydride-grafted copolymer had a density of 945 kg/m^3, an MI_5 of 0.12 g/10min and an HLMI of about 9 g/10min. The zinc content of the ionomer was 48.9 meq/kg, corresponding to a theoretical neutralisation level of about 127%. Similar ionomers are available from Solvay SA under the trade name Priex®.

The above ionomer was blended either with the natural fluff of a commercial Ziegler polyethylene pipe resin (resin A) available from BP Solvay as Eltex® 120N2025 made according to the general procedure described in EP 897934A, or with a second polyethylene resin (resin B or C) made using a metallocene catalyst, ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride, according to the general procedure described in WO 02/34829. The polyethylene resins were bimodal resins having the following general properties:

TABLE 1

Ziegler resin A

Bimodal resin	MI_5	g/10min	0.41
	HLMI	g/10min	11.8
	Density	kg/m^3	950.6
	SCB	Et/1000C	2.9

TABLE 2

Metallocene resin B

1st block	$MI_{2.16}$ (8/2)	g/10min	837
	Density	kg/m^3	974.5
	p1	%	0.60
2nd block	HLMI	g/10min	0.02
	SCB	C6/1000C	3.0
	Density	kg/m^3	919.2
	p2	%	0.40
Bimodal resin	MI_5	g/10min	0.18
	HLMI	g/10min	8.9
	Density	kg/m^3	954.2

TABLE 4

Metallocene resin C

1st block	$MI_{2.16}$ (8/1)	g/10min	39.7
	Density	kg/m^3	974.3
	p1	%	0.56
2nd block	HLMI	g/10min	0.02
	SCB	C6/1000C	2.0
	Density	kg/m^3	920.0
	p2	%	0.44
Bimodal resin	MI_5	g/10min	0.18
	HLMI	g/10min	7.1
	Density	kg/m^3	953.0

The blending of the ionomer and polyethylene resins was carried out in a lab-scale extruder (APV Baker under the trade name MP19TC25) at ~ 210°C, under nitrogen. A number of different blends were prepared, containing respectively 0%, 1.5%, 5%, 10%, and 20% ionomer plus the usual additives. The blends were then pelletized. Properties of the blends are shown in Tables 3 and 4 below.

TABLE 3

Blend 1: ionomer + Ziegler resin A

Irganox B225	3.5
Zn stearate (g/kg)	0.75
Ca stearate (g/kg)	0.25

TABLE 4

Blend 2: ionomer + metallocene resin B

Irganox B225	3.5
Zn stearate (g/kg)	0
Ca stearate (g/kg)	0

TABLE 4

Blend 3: ionomer + metallocene resin C

Irganox B225	3.5
Zn stearate (g/kg)	0
Ca stearate (g/kg)	0

EVALUATION OF BLENDS

For mechanical tests, pellets were compression-moulded into plaques at 15°C/min.

The density of the polyethylene is measured according to ISO 1183. HLMI is measured using the procedures of ASTM D-1238 at 190°C using a load of 21.6kg. MI_2 is measured using the procedures of ASTM D-1238 at 190°C using a load of 2.16kg. Density measurement on blends with Ziegler resin A have shown that density of the blends does not change at levels of up to 20 % weight of ionomer.

Capillary rheology was measured in a capillary rheometer, with a die having a ratio of length to internal diameter of either 30/2 or 0.2/2. μ_0 is the viscosity at a shear rate of 1 s^{-1}, and μ_2 the viscosity at a shear rate of 100 s^{-1}.

SOLID-STATE CREEP RESISTANCE

Creep tests were performed on Franck rig. Each creep station was equipped with an extensometer for strain measurements, placed in a temperature-controlled room. Creep test samples (in the shape of "dogbones") were formed from compression moulded rectangular plagues having a nominal thickness of about 2mm. The dimension of the dogbone test bars

was in accordance with ISO 527-2. The compression moulding conditions for the plaques were in accordance with ASTM D1928. In the testing, creep behaviour was monitored using the extensometer, and the percentage deformation over time recorded at a specific temperature and stress (23°C/12 MPa for resin A, 40°C/8.9 MPa for resin B, 40°C/9.2 MPa for resin C). The results for the three blends are shown in Figures 1 to 3, where it can be seen that addition of small amounts of ionomer results in a significant improvement, with the improvement being smaller at larger ionomer levels.

MOLTEN-STATE CREEP RECOVERY MEASUREMENTS

In the case of resin B, molten-state creep was also measured on a commercial Rheometrics SR-5000 at 190°C under a constant shear stress of either 200 or 300 Pa. The results are shown in Figure 4 in the form of a plot of normalised creep compliance as a function of time, where it can be seen that increasing levels of ionomer result in improved molten-state creep performance. This demonstrates that the resins of the invention can show improved resistance to creep in the molten state at low shear rates compared with known PE100 resins, which is especially important to control sagging during extrusion of large diameter pipes. Figure 5 shows the variation, with ionomer % weight, of normalized creep compliance measured at 1000 sec and also complex viscosity at 10^{-3} rad/s as calculated from experimental creep-recovery data, Fourier transform and Maxwell mode deconvolution as is known to those skilled in the art.

DYNAMIC RHEOMETRY

The determination of dynamic viscosity is made by using an oscillatory rheometer, preferably a Rheometric Scientific ARES rheometer. This method has been extensively described in the literature devoted to polymer rheology (see e.g. W.W. Graessley, Chapter 3 in Physical Properties of Polymers, 2nd Edition, ACS Professional Reference Book, Washington DC, 1993).

The measurements are performed on a Rheometric Scientific ARES rheometer between two 25 mm diameter plates; the gap between the plates is between 1 and 2 mm, and is thoroughly adapted according to the suitable thickness of the polymer sample once this latter has been inserted between the plates and warmed up to 190°C. The gap value is then recorded to be taken into account by the calculation software.

The sample is then temperature-conditioned for a period of 5 minutes before the measurement is started. The measurement is performed at 190°C. After temperature

conditioning, the measurement starts by applying an oscillatory strain $\gamma^*(\omega,t) = \gamma_M.e^{i\omega t}$, with a given amplitude γ_M and a given frequency ω to the bottom plate via a precision motor, whereas the top plate is kept fixed. The amplitude γ_M of this shear strain has been chosen in the linear zone of viscoelasticity of the polymer and is kept constant through the whole experiment. The oscillation frequency ω is varied through the range $[10^{-2} - 10^{+2}]$ radian/second. The oscillating shear strain is translated inside the material into an oscillating shear stress $\sigma^*(\omega,t)$, which in-phase and out-of-phase components are recorded as functions of the frequency ω, and used for the calculation of the complex modulus $G^*(\omega)$ as well as complex viscosity $\eta^*(\omega)$ of the polymer:

$$G^*(\omega) = \frac{\sigma^*(\omega,t)}{\gamma^*(\omega,t)} = G_m(\omega)\cdot e^{i\delta(\omega)} = G'(\omega) + i\cdot G''(\omega)$$

$$G_m(\omega) = \sqrt{G'^2(\omega) + G''^2(\omega)} \quad ; \quad \tan\delta(\omega) = \frac{G''(\omega)}{G'(\omega)}$$

$$\eta^*(\omega) = \eta'(\omega) - i\cdot\eta''(\omega) = \frac{G''(\omega)}{\omega} - i\cdot\frac{G'(\omega)}{\omega}$$

$$\|\eta^*(\omega)\| = \frac{\sqrt{G'^2(\omega) + G''^2(\omega)}}{\omega}$$

The results are shown in Figures 6 and 7 in the form of a plot of η^* versus ω. They show that even at 10% ionomer, the shear rheology is not adversely affected in any way, which means that such resins should extrude during pipe manufacture in the same way as resins containing no ionomer.

EXTENSIONAL RHEOMETRY

Extensional rheology performance is shown in Figures 8 and 9 as a plot of transient viscosity against time. This was measured on a commercial Rheometrics RME apparatus at 190°C at a Henky strain rate of either 0.1 or 1 s^{-1}. It shows an improvement at increasing levels of ionomer, corresponding to a higher melt strength even at low levels of ionomer, which can result in better processability.

Processability / Thermal Stability / Recyclability

Blending HDPE with ionomer in the amounts covered by the present invention does not induce any dramatic change in the melt viscosity with temperature throughout the whole normal melt processing window, either at the lower temperature limit or at the upper temperature limit. This is shown in Figures 10 and 11 by capillary rheology measurements.

The blends of the invention also show excellent thermal stability in the molten state: the value of dynamic viscosity at 10 rad/s and 190°C, as measured by dynamic rheometry on a blend of resin A + 10 % ionomer, does not vary by more than 1.5% over a period of 4 hours.

Blends of HDPE with ionomer according to the present invention can also be recycled and reprocessed. As is shown in Figure 12, such blends do not exhibit any significant change in rheological behaviour when pelletized up to 6 times, as indicated by the lack of any gels.

CLAIMS

1. Pressure pipe resin comprising from 90 to 99.9 wt%, based on the total weight of the resin, of a polyethylene, and from 0.1 to 10 wt%, based on the total weight of the blend, of an ionomer.

2. Pressure pipe resin according to claim 1 which is multimodal, preferably bimodal.

3. Pressure pipe resin according to claim 2 formed from a blend of (a) a polyethylene resin comprising from 35 to 60 wt% of a high molecular weight fraction having a density of up to 0.930 g/cm^3 and from 40 to 65 wt% of a low molecular weight fraction having a density of at least 0.965 g/cm^3, and (b) from 0.1 to 10 wt%, based on the total weight of the blend, of an ionomer..

4. Resin according to any preceding claim, wherein the quantity of ionomer in the blend is between 0.5 and 6 wt% based on the total weight of the blend, preferably between 1 and 5 wt%.

5. Resin according to claim 4, wherein the quantity of ionomer in the blend is between 1 and 2 wt% based on the total weight of the blend

6. Resin according to any preceding claim, wherein the ionomer is a grafted metal salt of an ethylene and maleic anhydride copolymer.

7. Resin according to any preceding claim, wherein the polyethylene resin comprises from 35 to 49 wt% of a first polyethylene fraction of high molecular weight, and from 51 to 65 wt% of a second polyethylene fraction of low molecular weight, the first polyethylene fraction comprising a linear low density polyethylene having a density of up to 0.928g/cm^3 and an HLMI of less than 0.6g/10min, and the second polyethylene fraction comprising a high density polyethylene having a density of at least 0.969g/cm^3 and an MI_2 of greater than 100g/10min, and the polyethylene resin having a density of greater than 0.940g/cm^3 and an

HLMI of from 1 to 100 g/10min.

8. Resin according to any of claims 1 to 6, wherein the polyethylene resin comprises from 44 to 56 wt% of a high molecular weight polyethylene fraction, and from 44 to 56 wt% of a low molecular weight polyethylene fraction;

the high molecular weight polyethylene fraction comprising a linear low density polyethylene having a density of from 0.913 to 0.923g/cm^3, and an HLMI of from 0.02 to 0.2 g/10min;

and the low molecular weight polyethylene fraction comprising a high density polyethylene having a density of at least 0.969 g/cm^3 and an MI_2 of greater than 100 g/10min,

wherein the relationship between the density D of the resin in g/cm^3 and the weight fraction of the low molecular weight fraction P_1 is defined by $0.055P_1 + 0.916 < D < 0.034P_1 + 0.937$.

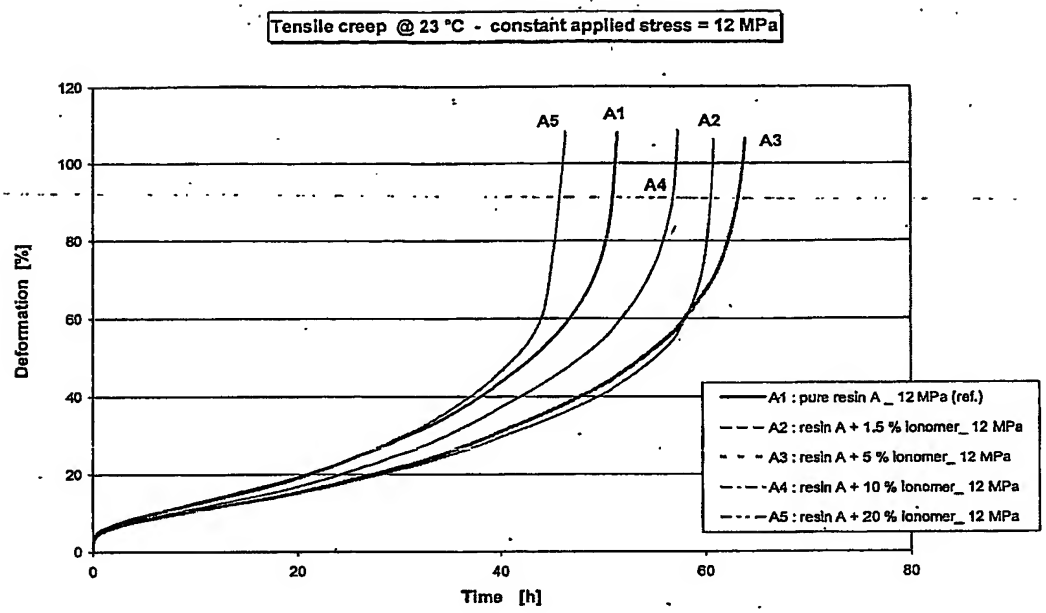

Figure 1

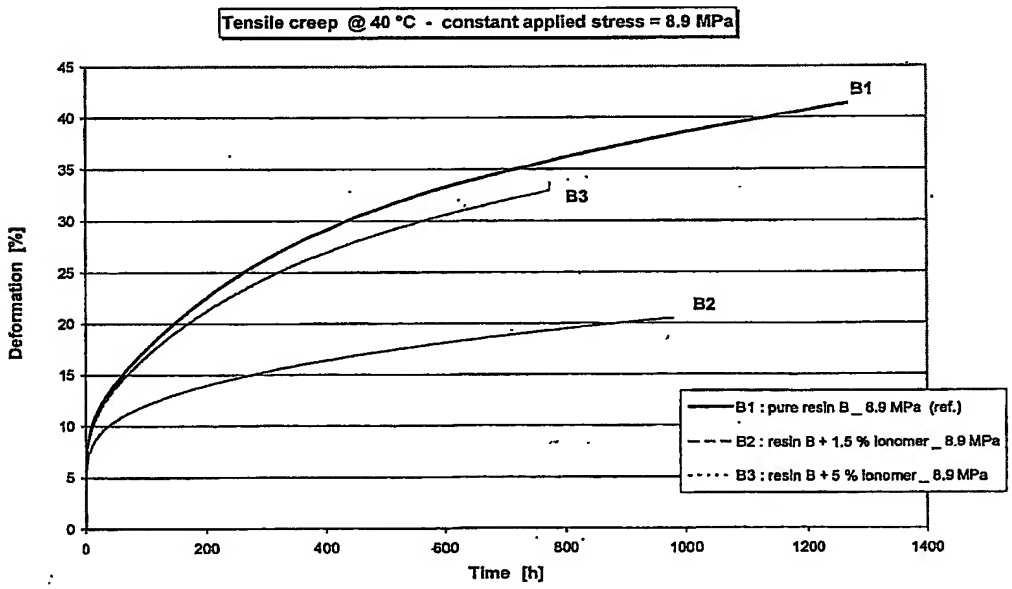

Figure 2

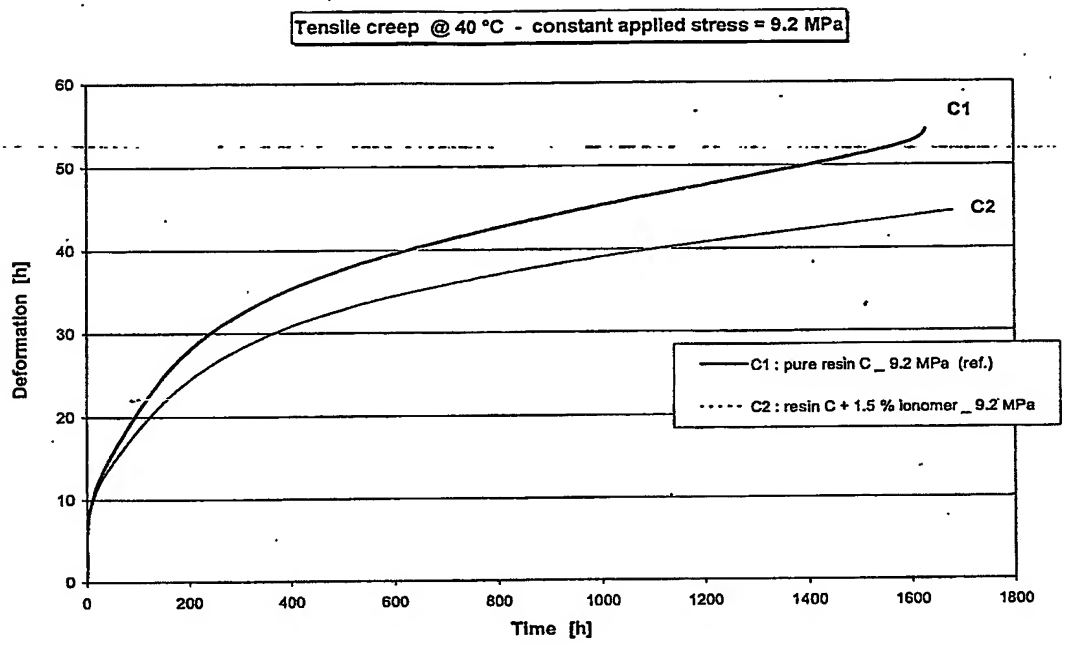
Tensile creep @ 40 °C - constant applied stress = 9.2 MPa
Deformation [h]
Time [h]
C1
C2
C1 : pure resin C _ 9.2 MPa (ref.)
C2 : resin C + 1.5 % Ionomer _ 9.2 MPa
0
10
20
30
40
50
60
0
200
400
600
800
1000
1200
1400
1600
1800

Figure 3

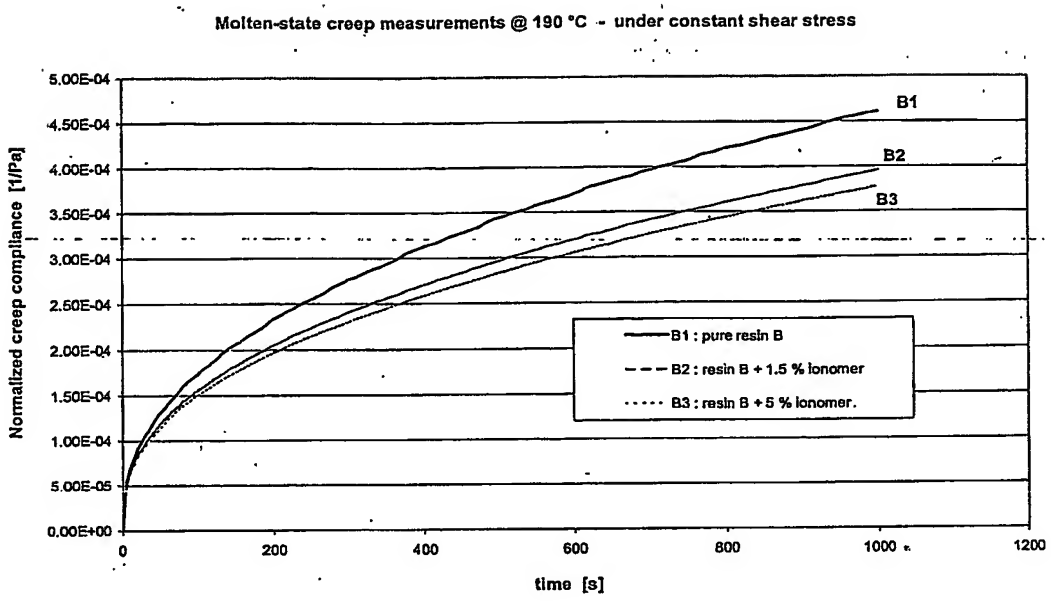

Figure 4

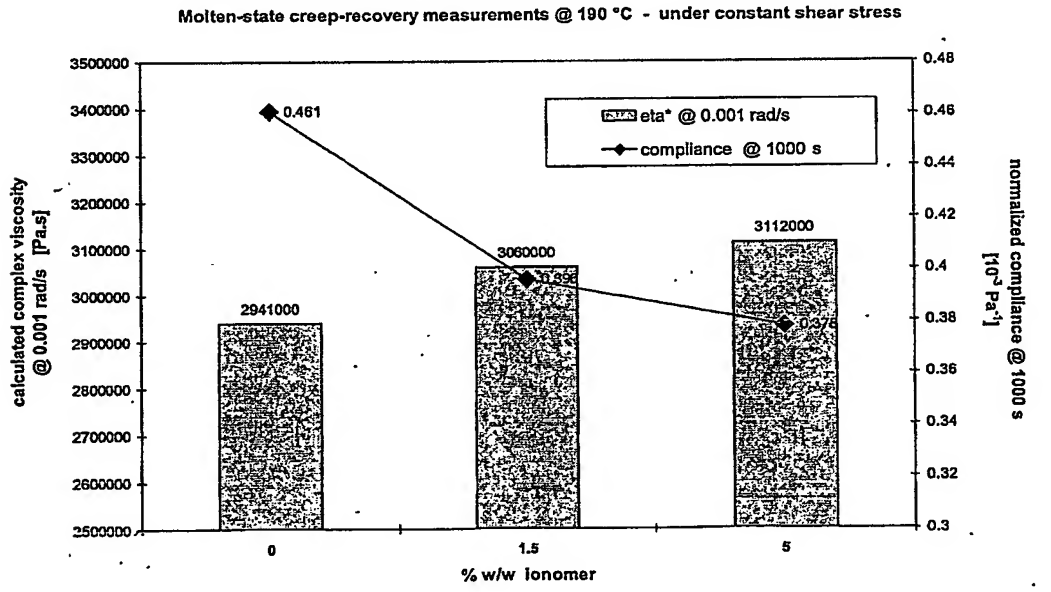

Figure 5

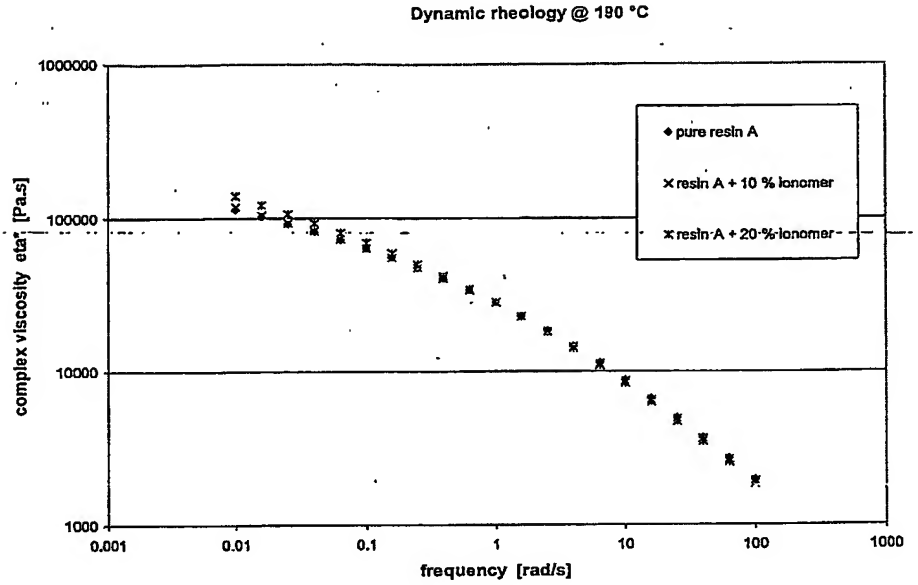

Figure 6

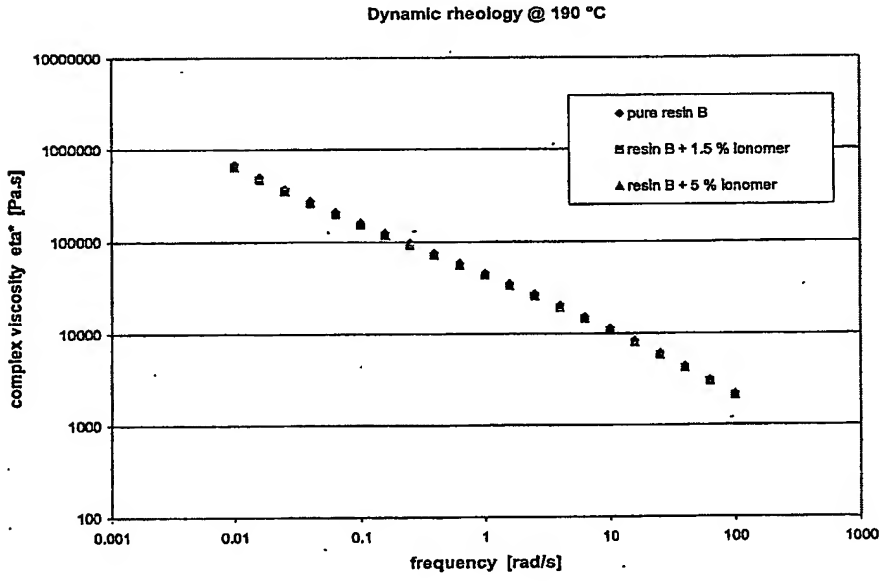

Figure 7

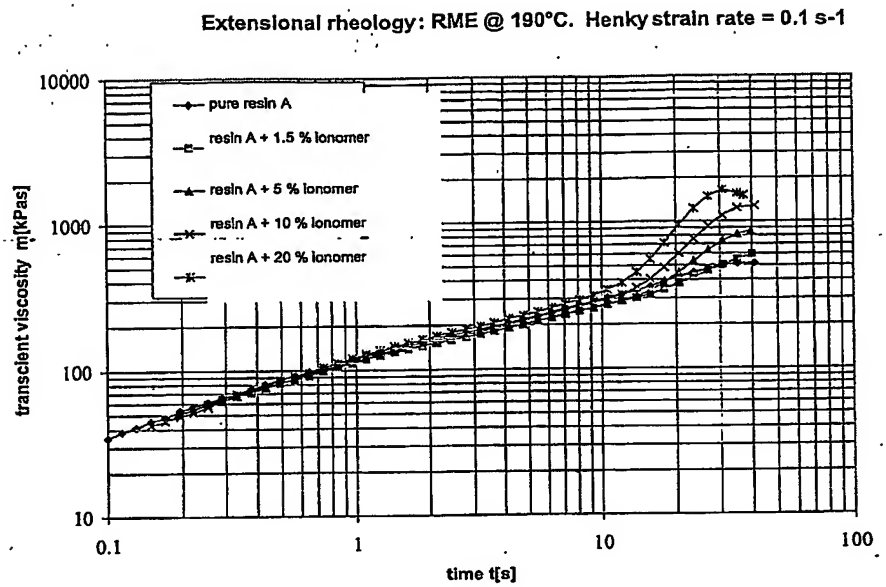

Figure 8

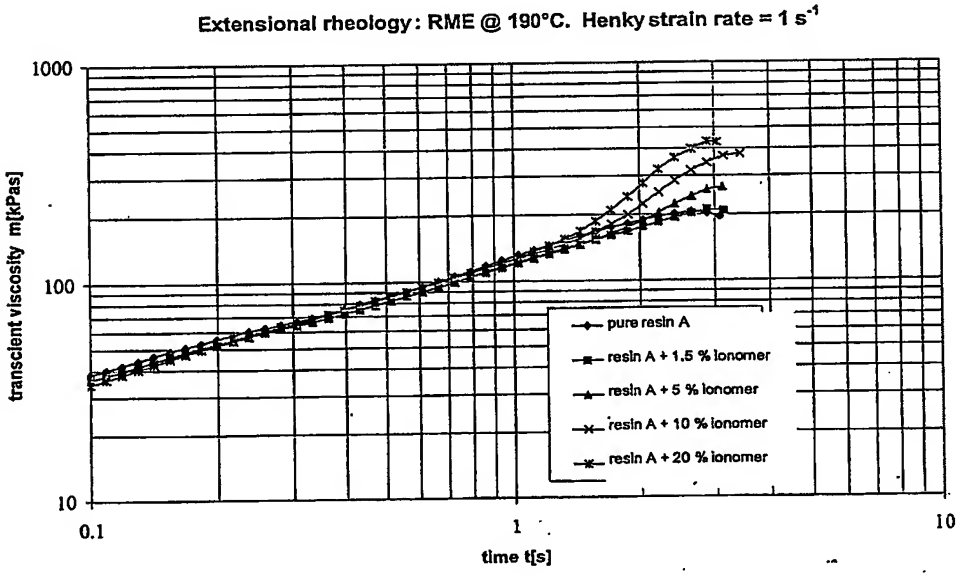

Figure 9

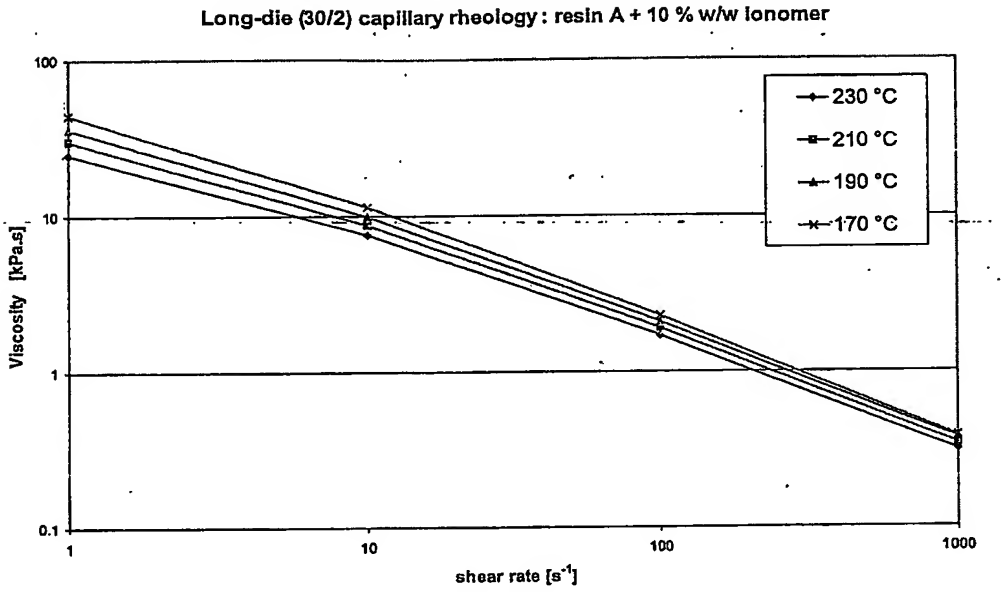

Figure 10

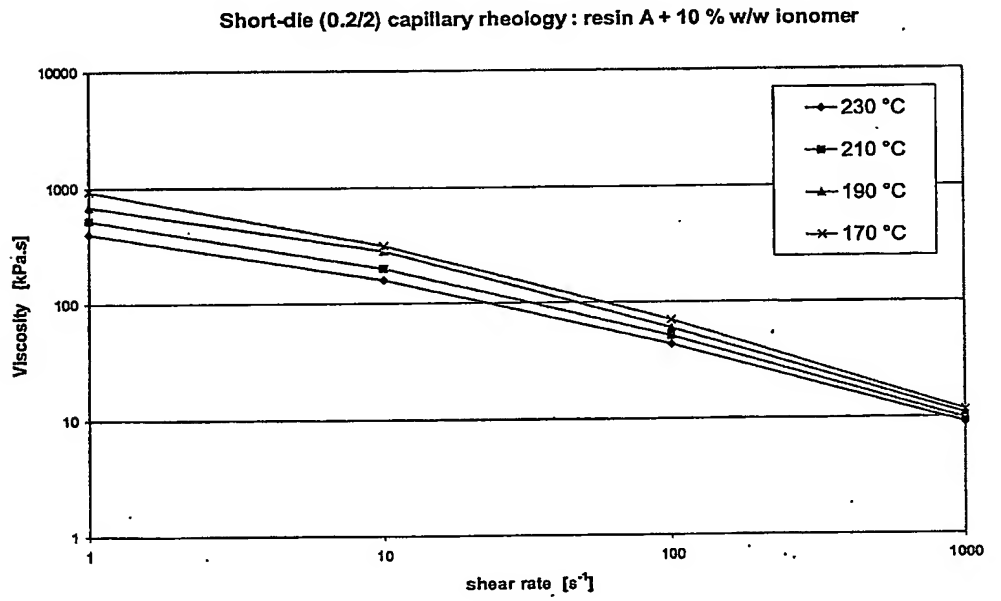

Figure 11

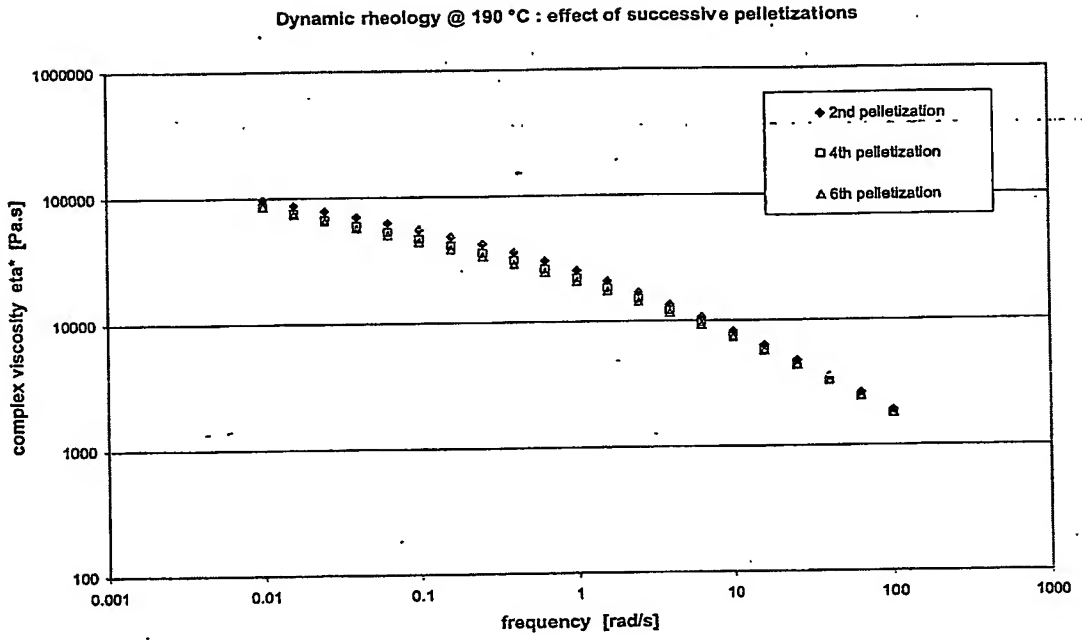
Dynamic rheology @ 190 °C : effect of successive pelletizations
complex viscosity eta* [Pa.s]
1000000
100000
10000
1000
100
0.001
0.01
0.1
1
10
100
1000
frequency [rad/s]
2nd pelletization
4th pelletization
6th pelletization

Figure 12

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☑ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☑ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.